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Surface properties of water soluble maltodextrin, starch acetates and starch acetates/alkenylsuccinates☆

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Abstract

Surface and interfacial tensions with hexadecane were measured for water soluble maltodextrin and starch ester solutions in order to determine their potential as stabilizers or emulsifiers. The surface tension for an acid hydrolysed starch (maltodextrin) initially declined with concentration and then reached an equilibrium value of 56 mN/m at 20–40 wt.%, suggesting that hydrated starch has this surface energy. Surface and interfacial tensions of starch acetates decreased more rapidly with concentration reaching values of 41–44 and 11–13 mN/m, respectively, at 40 wt.%. There was little dependence of surface or interfacial tensions on degree of substitution between 0.3 and 0.8 and amylose content of starch acetates. Surface and interfacial tensions for starch acetate/alkenylsuccinates were lower than those for starch acetates, particularly at low concentrations. Emulsions of soybean oil/water mixtures were stabilized for >1 day by waxy starch acetate/octenylsuccinate and acetate/dodecenylsuccinate but not starch acetates. In summary, these starch esters may represent biodegradable, economical alternatives to some emulsifiers and coating polymers currently in use.

Keywords: Surface; Interface; Starch; Acetate; Alkenylsuccinate; Emulsify

1. Introduction

Hydrophobically modified water soluble polymers are useful in a number of areas, such as thickeners, coatings, emulsion stabilizers and detergents [1–4]. The surface properties of these polymers are very important to their function of intermolecular adhesion, spreading on surfaces and dispersing oils and other hydrophobic compounds. There is interest in replacing non-degradable, petroleum based materials currently used with biobased materials derived from renewable feedstocks [5]. In particular, native and chemically modified starches have been prepared and studied for uses in these areas [6–10].

Surprisingly, there is relatively little published information on the surface and interfacial tensions of native and modified starches and existing data is conflicting or incomplete. Ray et al. [11] and Scholz et al. [12] determined critical surface tensions for wetting of 35–39 mN/m for starch, amylose and amylopectin films, 40 mN/m for amylose triacetate and approximately 32 mN/m for starch tributyrate. Lawton [13] reported contact angle data for various liquids on cast and extruded starch films and calculated surface energy values of 35–42 mN/m using the harmonic mean method of Wu and Brzozowski [14,15]. Using the same data and the van Oss/Chaudhury/Good (VCG) method, Biresaw and Carriere [16] calculated a value of 43 mN/m. Surface energies of 47–56 mN/m were reported by Odidi et al. [17] for discs made from compressed starch powder although surface roughness would be expected to influence the results. Krycer and Pope [18] measured a surface tension of 59 mN/m for a 4% solution of corn starch in water. Rudoph and Glowaky [19] found surface tensions of 36–60 mN/m for dilute (1%) aqueous solutions of mixed (acetate/phthalate, propionate/phthalate, butyrate/phthalate) esters of hydrolyzed starches of degree of substitution (DS) 1.5–2.3 [19]. Interfacial tensions of 12–21 mN/m were reported recently by Tesch et al. [7] for

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product and the use of the name by the USDA implies on approval of the product to the exclusion of others than may be suitable.

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1–5% solutions of octenylsuccinate (OSA) starch and vegetable oil but no information on the DS, molecular weight or preparation method for the OSA starch was given. There have been no published reports on the surface properties of starch acetates of DS < 3 or mixed acetate/alkenylsuccinate esters of starch.

In summary, the surface energy of starch is uncertain and there is little data or understanding of the effects of DS and concentration on the surface properties of starch derivatives. Part of the reason for this may be that most commercially available derivatives are low DS (<0.05) granular starches which tend to have poor solubility in water or other solvents. Recently, Shogren and Biswas [20] reported a simple method for preparation of highly water soluble starch acetates and mixed esters using microwave heating under non-aqueous, homogeneous conditions. The purpose of this study was to characterize the effects of acetate and alkenylsuccinate groups on the surface and interfacial tensions of aqueous starch solutions and thus better understand structure/property relations and help to determine feasibility of certain applications.

2. Experimental

2.1. Materials

Normal corn starch (pure food grade), waxy maize starch (7350) and maltodextrin (Star-dri 1) were purchased from Tate & Lyle (Decatur, IL). The dextrose equivalent (DE) of the maltodextrin was one. High (70%) amylose starch (Hylon 7) was purchased from National Starch (Bridgewater, NJ). Starches were vacuum dried overnight at 110 °C before using. Glacial acetic acid, acetic anhydride (>99%), octenylsuccinic anhydride (OSA, 97%), dodecenylsuccinic anhydride (DDSA, 95%) and hexadecane (>99%) were purchased from Aldrich Chemical Co. Refined soybean oil was purchased from Alnoroil Co. (Valley Stream, NY). Oil red O and Tween 20 (polyoxyethylene sorbitan monolaurate) were purchased from Sigma Chemical Co.

2.2. Preparation of starch esters

The basic procedure has been described previously [20]. Typically, 70 g dry starch, 70 g acetic acid, 7–35 g acetic anhydride, 0–7 g OSA or 0–8.8 g DDSA were added to a 270 ml Teflon vessel. A magnetic stir bar was added and the mixture was stirred for 5 min. The vessel was then sealed, the thermocouple inserted and the vessel was heated in a Milestone Microwave Labstation 1600 (Milestone Inc., Shelton, CT) from 25 to 150 °C over 3.5 min, then 150–160 °C over 1.5–2.5 min. After opening the reactor, the contents were placed in a Waring blender with 400 ml ethanol (99.5%) and blended until the precipitate was broken into fine particles (∼1 min). The ethanol supernatant was poured off and four additional ethanol extractions were performed. Excess ethanol was removed by filtration on a buchner funnel, and the starch ester was dried in a forced air oven overnight at 50 °C and then in a vacuum oven overnight at 80 °C.

2.3. Analyses

Degree of substitution values were estimated using ^{1}H NMR [21]. Briefly, samples (2%) were dissolved and hydrolysed in 0.5 M NaOD and areas of acetyl CH_3 or methyl CH_3 and starch CH resonances were measured. DS represents the average number of substituent functional groups per glucose residue. Water solubilities were determined by stirring 0.5 g sample in 30 ml water at room temperature, centrifuging at 3000 rpm for 10 min, drying and weighing the supernatant. Intrinsic viscosities were measured on deacylated samples in 1 M KOH as described previously [20].

2.4. Surface and interfacial tension measurement

Dynamic surface and interfacial tension measurements were conducted using axisymmetric drop shape analysis method [22] on a FTA-200 automated goniometer (First Ten Angstroms, Portsmouth, VA) equipped with the fta32 v2.0 software. The main features of the instrument are: an automated pump that can be fitted with various sizes of syringes and needles to allow for control of pendant drop formation; an automated image viewing and capturing system with various image capture triggering options; software for an automated drop shape analysis of the captured drop image, and for measuring the surface/interfacial tension; computer hardware and software for data capture, storage, analysis, and transfer. All measurements were conducted at room temperature (23 ± 2 °C). In a typical procedure, a 10 ml disposable syringe equipped with a 17 gauge (1.499 mm o.d.) blunt disposable needle (KDS 17-1P, Kahnetics Dispensing Systems, Bloomington, CA 92316) was used to generate a pendant drop of the starch solution in air or hexadecane medium contained in a glass cuvette (10 mm). The instrument is programmed to automatically deliver a specified volume of the starch solution at 1 μL/s, and also to automatically trigger image capture when the pump stops. All runs were programmed to acquire images at a rate of 0.067 s/image, with a predetermined trigger period multiplier to allow for a total of 35 images to be captured during the acquisition period. At the end of the acquisition period, each image was automatically analyzed, saved, and a plot of time versus surface or interfacial tension displayed. Repeat measurements (2–4) were conducted on each sample from which equilibrium surface or interfacial tension values were obtained by averaging the values at very long periods, where the surface and interfacial tension values showed little or no change with time. Prior to running tests with the starch solutions, the instrument was calibrated with water and then checked by measuring the interfacial tension between water and pure hexadecane.

2.5. Emulsification assay

The method was adapted from Srokova et al. [9]. Emulsions were prepared by blending 10 ml soybean oil stained with Oil red O, 90 ml water and 0.5 g emulsifier in a Waring blender for 30 s at 22,000 rpm. Emulsions were then poured into 250 ml graduated cylinders and volumes of separated oil and cream phases after 1 min, 1 h and 24 h were measured.

Table 1
Composition and properties of starch acetates and starch acetate/alkenylsuccinates used for surface and interfacial tension measurements

Base starch	Amylose (%)	DS acetate	DS OSA	DS DDSA	Water solubility (%)	Intrinsic viscosity (ml/g)[a]
Maltodextrin	27	0			99	26
Waxy maize	1	0.35			97	17 (178)
Waxy maize	1	0.70			99	22
Waxy maize	1	0.36	0.046		91	17
Waxy maize	1	0.31		0.022	91	18
Waxy maize	1		0.030[b]		25[c]	175
Normal corn	27	0.78			95	46 (160)
High amylose corn	70	0.57			70	59 (120)

OSA, octenylsuccinate; DDSA, dodecenylsuccinate.
[a] Values in parentheses are for native (unmodified) starches.
[b] Made using aqueous dispersion reaction [23].
[c] Sample heated at 140 °C.

3. Results and discussion

3.1. Synthesis and solubility in water

Compositions of the starch esters are given in Table 1. The chemical structures of the starch esters are given in Fig. 1. Acetylation efficiencies were high, typically 100% or higher, as reported previously [20]. Values over 100% reflect direct esterification with acetic acid in addition to reaction with acetic anhydride. Reaction efficiencies of OSA (55%) and DDSA (29%) were lower, reflecting the slower rates of reaction of starch with alkenylsuccinic anhydrides. Water solubilities of the samples were >95% (w/w) except for high amylose starch acetate which was 70%. For comparison, the water solubility of an OSA starch of degree of substitution 0.03 prepared by the aqueous suspension method [23] was only 25%, even with prior heating and stirring an aqueous solution to 140 °C in a sealed reactivial. Intrinsic viscosities were low for waxy maize starch and increased with amylose content as noted previously [20].

3.2. Surface and interfacial tension

As an example, data from of a typical duplicate measurement of dynamic surface tension for waxy starch acetate, DS 0.35, is illustrated in Fig. 2. The decline in apparent surface tension with time is likely due to diffusion of starch acetate molecules to the air interface.

The effects of concentration on the surface and interfacial tensions of a low molecular weight starch (maltodextrin) and starch esters are shown in Figs. 3 and 4, respectively. The data indicate that all the starches investigated were surface active, as demonstrated by their ability to lower the surface tension of water and the interfacial tension of water/hexadecane. In all cases, the surface and interfacial tensions decreased with increasing

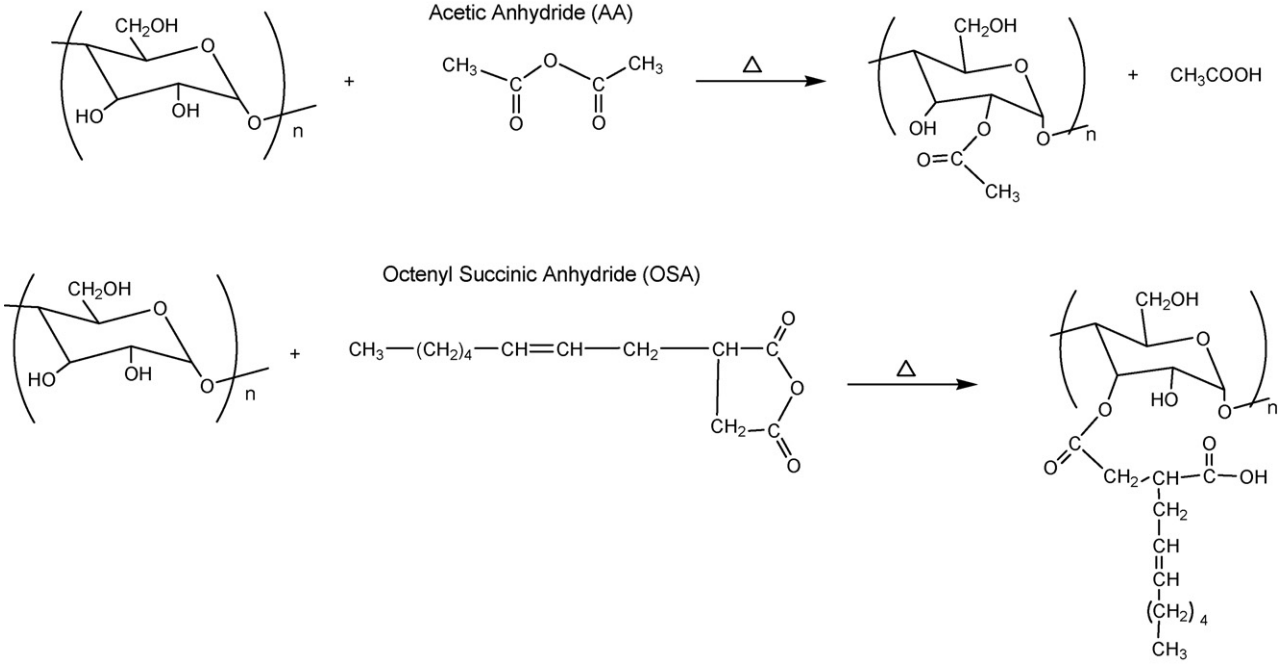

Fig. 1. Esterfication of starch with anhydrides. DDSA starch (not shown) is similar to OSA starch except $n = 8$. Esterification can occur at the 2, 3 or 6 hydroxyl positions.

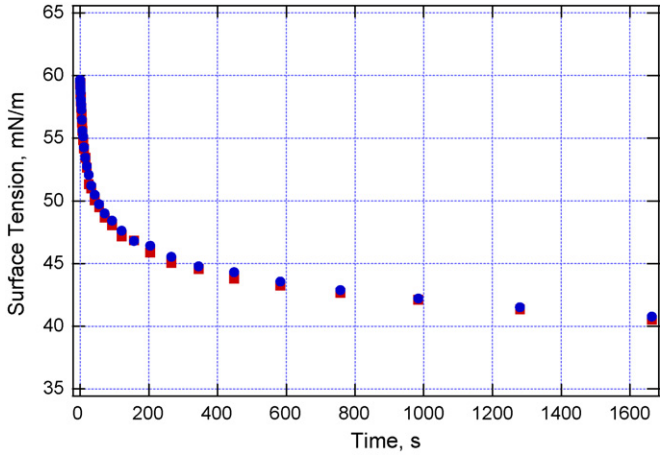

Fig. 2. Duplicate measurements of dynamic surface tension for 20% aqueous solution of waxy starch acetate (DS = 0.35).

concentration of the maltodextrin in water, reaching a constant value at high concentrations (Table 2). Such results are an indication of increased surface concentration and eventual saturation of the interface by the starch molecules as a function of starch concentration in water.

Surface tension for the maltodextrin sample decreases gradually with increase in concentration, reaching a constant value of 56 ± 1 mN/m at 20–40%. This would suggest a value of 56 mN/m for the surface energy of starch in a hydrated state. This is similar to a value of 59 mN/m estimated using Sugden's group contribution theory [24,25] using a starch density of 1.5 but much higher than values of 35–43 mN/m found by contact angle methods [11,13,16]. The reason for this is probably the extensive contamination of solid starch surfaces with hydrophobic compounds as shown by XPS of native [26] and extruded starches [27]. These compounds include silicon oils, hydrocarbon greases, and native starch lipids and proteins. The lipid and protein composition of corn starches has been reported [28]. Such adsorption of hydrophobic substances onto starch surfaces would tend to give lower surface energy values than for a pure starch surface. Indeed, surface energies for starch as low as 35 mN/m are similar to that found for polyethylene and suggest coverage of starch surfaces by a monolayer of hydropho-

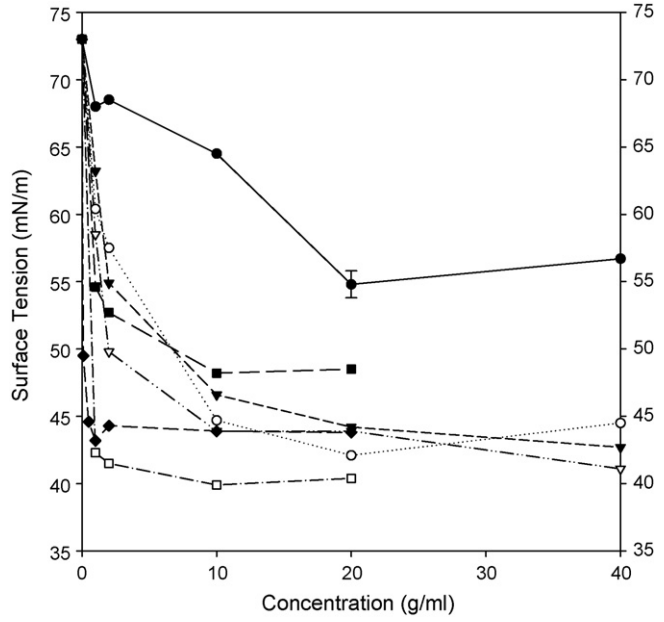

Fig. 3. Effect of concentration on the surface tensions of aqueous solutions of maltodextrin, starch acetates and starch acetate/alkenylsuccinate. Maltodextrin (●), waxy acetate DS 0.35 (◯), waxy acetate DS 0.70 (▼), normal acetate DS 0.78 (▽), high amylose acetate DS 0.57 (■), waxy acetate/OSA DS 0.35/0.042 (□), waxy acetate/DDSA, DS 0.31/0.022 (⧫).

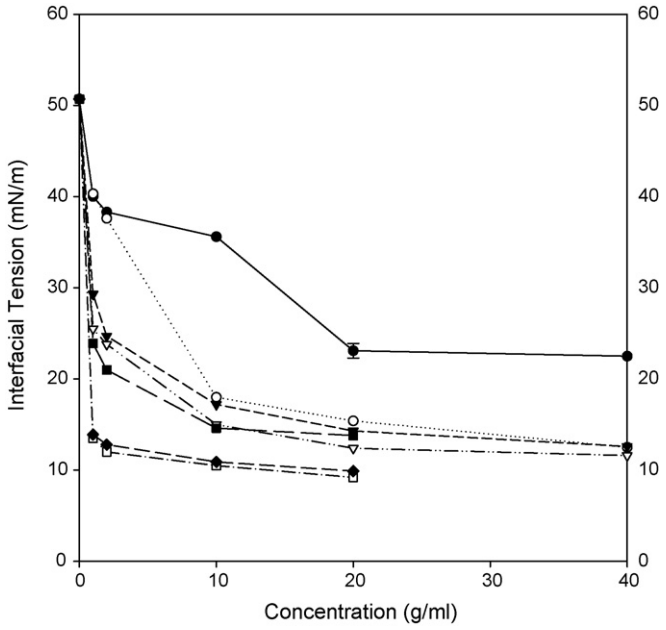

Fig. 4. Effect of concentration on the interfacial tensions of aqueous solutions of maltodextrin, starch acetates and starch acetate/alkenylsuccinate with hexadecane. Maltodextrin (●), waxy acetate DS 0.35 (◯), waxy acetate DS 0.70 (▼), normal acetate DS 0.78 (▽), high amylose acetate DS 0.57 (■), waxy acetate/OSA DS 0.35/0.042 (□), waxy acetate/DDSA, DS 0.31/0.022 (⧫).

Table 2
Equilibrium surface tensions for modified starches: comparison among experimental, literature and calculated values

Starch[a]	Equilibrium surface tension[b] (mN/m)		
	This work	Literature	Calculated[c]
MD0.0	56 ± 1	35–39[d], 35–43[e], 47–56[f]	59
WM0.35	44		
WM0.70	43	40[g]	46[h]
NC0.78	41		
HA0.57	48		
WM0.36/0.046	40		
WM0.31/0.022	43		

[a] MD, maltodextrin; WM, waxy maize; NC, normal corn; HA, high amylose corn; numbers refer to DS.
[b] Values obtained at the highest concentrations measured.
[c] Calculated using group contribution (parachor) method [24,25].
[d] Ray et al. [11].
[e] Lawton [13] and Biresaw and Carriere [16].
[f] Odidi et al. [17].
[g] Value given is for amylose triacetate (Scholz et al. [12]).
[h] Value calculated for starch triacetate.

bic material. Since a new surface is created during the dynamic drop shape analysis used here, there may be less surface contamination and hence a truer estimate of the surface tension for starch.

Surface tensions for starch acetates declined more rapidly with concentration than starch presumably due to the lower surface free energy of acetate group versus the hydroxyl groups of starch. Limiting values of surface and interfacial tensions of 41–44 and 11–14 mN/m, respectively, were obtained for all of the starch acetates at concentrations above 20%. Interestingly, there was no significant effect of DS on surface or interfacial tension in the DS range of 0.3–0.8. This suggests that starch molecules can adopt orientations which give high surface concentrations of acetate groups regardless of DS. Calculation of the surface energy of starch triacetate by the group contribution method of Sugden et al. [24,25] using a density of 1.35 g/cm^3 [29] gives a value of 46 mN/m. This is reasonably close to the surface tensions measured for starch acetates and further supports the idea that acetylated areas of starch congregate near the air interface. Surface tensions for the DS 0.3–0.8 starch acetates were also close to critical surface tensions for liquid spreading of 40 mN/m measured for amylose triacetate [12]. There was no significant difference in surfaces tensions between the different types of starch except perhaps high amylose starch acetate which had higher surface tensions at 20% concentration likely due to its incomplete solubility.

Addition of just a small number (DS 0.02–0.04) of OSA or DDSA groups to starch causes a very rapid decline in surface and interfacial tensions to 42–43 and 13–14 mN/m, respectively, at 1% concentration. Little further change was noted at higher concentrations. This indicates a large equilibrium constant for the surface versus bulk states and hence a much smaller free energy for the alkenylsuccinate groups on the surface. This is commonly called the hydrophobic effect and is considered to be due to ordering of water molecules around the hydrocarbon groups giving a decrease in entropy. Interfacial tensions described above were lower than those measured previously (18–21 mN/m) for 1% solutions of commercial OSA starches/vegetable oil [7]. It is difficult to interpret these differences, however, because the DS of the commercial starches was not reported.

Interfacial tensions can be predicted using a number of empirical and theoretical expressions. In general, interfacial tension is given as:

$$\gamma_{AB} = \gamma_A + \gamma_B - W_a \quad (1)$$

where W_a is the work required to separate the two liquids. A simple empirical rule from Antonow [30,31] states that

$$\gamma_{AB} = |\gamma_A - \gamma_B| \quad (2)$$

This equation is thought to apply when a monolayer of liquid B (the one of lower surface tension) forms on the surface of liquid A [32]. In this case, $W_a = 2\gamma_B$ and Eq. (1) reduces to Eq. (2). Alternatively, if it is assumed that W_a can be regarded as a sum of dispersive and polar contributions, then two approximate relations can be derived. The harmonic mean equation (HM) [15]

$$\gamma_{AB} = \gamma_A + \gamma_B - 4\gamma_A^d \frac{\gamma_B^d}{\gamma_A^d + \gamma_B^d} - 4\gamma_A^p \frac{\gamma_B^p}{\gamma_A^p + \gamma_B^p} \quad (3)$$

is considered useful for interfaces between low energy fluids. The geometric mean equation (GM)

$$\gamma_{AB} = \gamma_A + \gamma_B - 2(\gamma_A^d \gamma_B^d)^{1/2} - 2(\gamma_A^p \gamma_B^p)^{1/2} \quad (4)$$

is preferred for interfaces between high and low energy materials [33]. The γ^d values for starch were estimated based on literature X_d values, which were in the range 0.73–0.98 [13,16]. X_d is defined as $X_d = \gamma^d/\gamma^t$ [14] where γ^d and γ^t are dispersive and total surface energy, respectively.

The results in Table 3 show that, except for WM0.31/0.022, the calculations predicted the correct trend, regardless of the calculation method. Antonow's method predicted values that were rather similar to albeit slightly larger than the measured ones for starch acetates and maltodextrin. Good agreement with

Table 3
Measured vs. calculated hexadecane-modified starch interfacial tension (mN/m)

Starch[a]	Measured	Calculated[b]						
		Ant[c]	GM-80[d]	HM-80[e]	GM-70[f]	HM-70[g]	GM-60[h]	HM-60[i]
WM0.36/0.046	9.2	12.5	8.2	8.3	12.0	12.0	16.1	16.2
NC0.78	12	13.5	8.4	8.7	12.3	12.3	16.5	16.6
WM0.31/0.022	9.9	15.5	9.0	9.4	13.0	13.0	17.2	17.3
WM0.70	13	15.5	9.0	9.4	13.0	13.0	17.2	17.3
WM0.35	13	16.5	9.3	9.7	13.3	13.4	17.6	17.6
HA0.57	14	20.5	10.5	11.4	14.7	15.0	19.2	19.2
MD0.0	23	28.5	13.3	15.3	17.8	18.9	22.7	23.0

[a] MD, maltodextrin; WM, waxy maize; NC, normal corn; HA, high amylose corn; numbers refer to DS.
[b] For hexadecane, $\gamma^t = \gamma^d = 27.5$ mN/m [41].
[c] Antonow's method [28].
[d] Geometric mean method using $X_d = \gamma^d/\gamma^t = 0.80$.
[e] Harmonic mean method using $X_d = \gamma^d/\gamma^t = 0.80$.
[f] Geometric mean method using $X_d = \gamma^d/\gamma^t = 0.70$.
[g] Harmonic mean method using $X_d = \gamma^d/\gamma^t = 0.70$.
[h] Geometric mean method using $X_d = \gamma^d/\gamma^t = 0.60$.
[i] Harmonic mean method using $X_d = \gamma^d/\gamma^t = 0.60$.

Table 4
Emulsification of soybean oil/water with waxy maize starch acetates and acetates/alkenylsuccinates

DS acetate	DS, ASA	Oil/cream volumes (ml)		
		1 min	1 h	24 h
0[a]		7/0	7/7	10/0
0.35		5/0	9/0	10/0
0.35	0.042 OSA	0/0	1/0	1/10
0.31	0.022, DDSA	0/0	0/0	0/10
0	0.030 OSA[b]	0/60	0/40	0/30
Tween 20		0/0	1/0	1/10

[a] Control sample (oil, water only).
[b] Aqueous dispersion reaction [23].

Antonow's rule has also been obtained for poly(ethylene glycols) and *n*-alkanes [34]. For starch esters containing OSA and DDSA, the GM and HM calculations using $X_d = 0.80$ predicted interfacial tension values close to those observed. Such a large dispersive component is consistent with the tendency of the hydrophobic OSA and DDSA groups to orient towards the interface. For starch acetates and maltodextrin, GM and HM calculations using $X_d = 0.70$ and $X_d = 0.60$, respectively, predicted interfacial tension values close to those observed. These results are consistent with the more polar nature of the hydroxyl groups of starch. Literature values for X_d for starch range from 0.73 to 0.98 and probably reflect starch surfaces which have variable amounts of hydrophobic compounds covering the surface. Such behavior is common among high surface energy materials. It should be noted that the presence of water was not taken into account in the above analysis and that this could give lower values of X_d than those anticipated for pure starch.

3.3. Emulsification properties

Emulsification activities for starch esters and Tween 20, a typical synthetic surfactant at 0.5 wt.%, are shown in Table 4. Oil and water separated rapidly for the control test (no added surfactant) and also for the waxy maize starch acetate. The waxy starch acetate/alkenylsuccinate samples, however showed very slow oil/water separation similar to the Tween 20. This contrasts with OSA starch prepared by the aqueous reaction which exhibits rapid separation of a large cream phase.

Based on previous studies of aqueous suspension starch reactions [35,36], it is likely that substitution occurs near the branch points of amylopectin molecules which occur in the amorphous regions of the starch granule. This substitution pattern probably results in highly hydrophobic regions which self associate strongly and become "buried", limiting solubility and emulsification activity. Solubility in water is low for the OSA starch made by aqueous suspension reaction (Table 1) so that less would be available to emulsify. For the starch esters made by the homogeneous microwave reaction, there is probably a more random distribution of substituents over the whole starch molecule thus opening up the conformation to interaction with water and other hydrophobes. Intrisinic viscosities and hence molecular weights are much lower for the microwave synthesized starch esters than those made by aqueous suspension reaction (Table 1). These lower molecular weights also probably improve solubility as well as the rate at which OSA starch can diffuse to the oil/water interface.

4. Conclusions

Values for the surface energy of starch and starch acetates of 56 and 42 mN/m were determined from asymptotic values of surface tension at high concentrations. These were in fairly good agreement with values calculated based on group contribution theory for starch and starch triacetate. This indicates that only rather low acetate DS is needed to cause the same surface tension lowering as for the triacetate. This information should be useful for predicting compatibility of starch with other polymers and fillers in composites, and predicting spreading of starch solutions on different substrates. Mixed starch acetate/alkenylsuccinate esters showed low water/hexadecane interfacial tensions, high water solubility, good emulsification and were prepared in a single easy step. Currently, starch alkenylsuccinates are prepared by the aqueous slurry method then have to be hydrolysed to improve solubility and emulsification [37]. Many starch esters of low to moderate DS have been found to be biodegradable [38–40], so it would be anticipated that the starch esters described in this work would also be biodegradable.

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